AD-A053 768 ARMY MEDICAL BIOENGINEERING RESEARCH AND DEVELOPMENT --ETC F/G 7/3
MECHANISM OF THE REACTION OF BROMINE AND POLYHYDRIC PHENOLS TO --ETC(U)
APR 78 W F COWEN, D H ROSENBLATT, C W WADE

UNCLASSIFIED USAMBRDL-TR-7806 NL

| OF |
AD
A053768

END
DATE
FILMED
6 -78
DDC

AD

(12)

TECHNICAL REPORT 7806

MECHANISM OF THE REACTION OF BROMINE AND POLYHYDRIC PHENOLS TO FORM BROMINATED METHANE COMPOUNDS: BROMINATION OF DIMEDONE

WILLIAM F. COWEN, Ph.D.
DAVID H. ROSENBLATT, Ph.D.
CLARENCE W.R. WADE, Ph.D.

US ARMY MEDICAL BIOENGINEERING RESEARCH and DEVELOPMENT LABORATORY
Fort Detrick
Frederick, Md. 21701

APRIL 1978

US ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
FORRESTAL BUILDING
WASHINGTON, DC 20314

NOTICE

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: TECHNICAL REPORT 7806 ✓
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): MECHANISM OF THE REACTION OF BROMINE AND POLYHYDRIC PHENOLS TO FORM BROMINATED METHANE COMPOUNDS: BROMINATION OF DIMEDONE.

5. TYPE OF REPORT & PERIOD COVERED: Final Report. March 1976 - November 1977.

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s): WILLIAM F. COWEN, Ph.D.
DAVID H. ROSENBLATT, Ph.D.
CLARENCE W.R. WADE, Ph.D.

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS: US Army Medical Bioengineering Research & Development Laboratory, ATTN: SGRD-UBG, Fort Detrick, Frederick, MD 21701

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 61101A 3A161101A91C/00/302

11. CONTROLLING OFFICE NAME AND ADDRESS: US Army Medical Research & Development Command, ATTN: SGRD-AJ, Fort Detrick, Frederick, MD 21701

12. REPORT DATE: April 1978

13. NUMBER OF PAGES: 29 (12) 31p.

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): USAMBRDL-TR-7806

15. SECURITY CLASS. (of this report): UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Bromination
Polyhydric phenols
Water analysis
Water, drinking

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Treatment of dimedone with bromine in aqueous solution resulted in the formation of monobromodimedone, dibromodimedone, and bromoform along with lesser amounts of dibromomethane. At a 1:1 ratio of bromine to dimedone at 25°C and pH 7, the production of bromoform was about 0.057 percent of theory. At a bromine:dimedone ratio of 2:1 the yield of bromoform was increased to 16 percent of theory. Dibromodimedone (10^{-5} M) in water at pH values from 6 to 7.5 did not produce measurable dibromomethane, while bromoform production was

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

407 838

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

JOB

20. Abstract (continued)

undetectable at pH 6 and increased with increasing pH. In these tests, monobromodimedone was also shown to form more readily at higher pH values. These results support the reaction mechanisms published for chlorination of humic-type substances except that formation of dibromomethane should be considered a minor reaction pathway at pH 6 to 7.5.

TABLE OF CONTENTS

TABLE

FIGURES

INTRODUCTION

This research project was established to investigate the mechanisms by which aqueous bromine solutions react with polyhydric phenols to form brominated methane compounds. An analytical procedure was successfully established, based on procedures developed at the U.S. Environmental Protection Agency,[1] to determine the methane compounds. In spite of the increasing work load from other projects, a few significant preliminary experiments were performed before this project had to be terminated.

This report is a summary of the significant literature accumulated for the research protocol, the detailed methodology employed in conducting the bromination test and gas chromatographic analyses, and the results of reactions between bromine and dimedone and between dibromodimedone and water. It is hoped that even such a limited summary report may be of value to future research at USAMBRDL in the areas of halogenation and trace organic analysis.

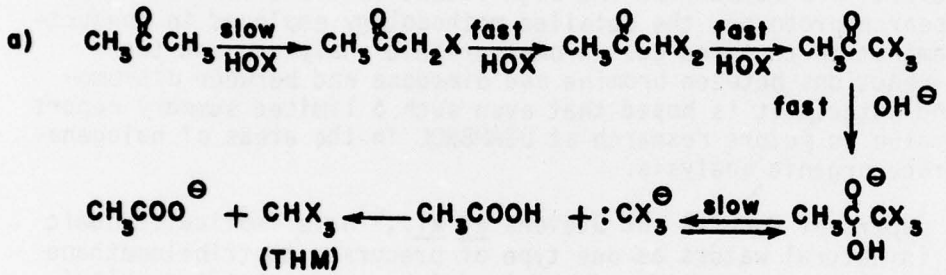
Recent papers of Rook[2,3] and Stevens et al.,[4] have implicated humic substances in natural waters as one type of precursor to trihalomethane (THM), i.e., haloform compounds, found in drinking waters after chlorination (Table 1).[5-9]

TABLE 1. PRINCIPAL TRIHALOMETHANE COMPOUNDS FOUND IN EPA NORS DRINKING WATER STUDY[7]

Compound	Median Concentration in Finished Water (µg/l)
Chloroform, $CHCl_3$	21.0
Bromodichloromethane, $CHBrCl_2$	6.0
Dibromochloromethane, $CHBr_2Cl$	1.2
Bromoform, $CHBr_3$	<5.0

Trihalomethane compounds are known to result from the classical haloform reaction (Fig. 1 (a)) between a halogen and an acetyl ($CH_3-\overset{O}{\overset{\|}{C}}-$) group attached either to carbon or hydrogen. The reaction can also occur with groups which are oxidizable to the acetyl structure by the halogen. Even

these descriptions are apparently too strict, because as Booth and Saunders[10] have demonstrated, the iodoform reaction also occurs with quinones, catechol, resorcinol, and dimedone (Fig. 2), compounds that do not possess an acetyl group bound to carbon or hydrogen. Since all of these compounds resemble one or another of the aromatic, polyhydric and polyketo building blocks of humic acids, their participation in the haloform reaction supports the thesis of Rook and of Stevens et al., that humic substances may be precursors of THM in drinking water.



b) Oxidation of halogens during chlorination

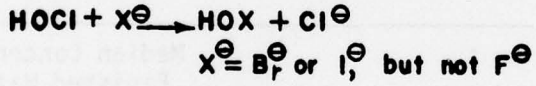


Figure 1. Haloform Reaction.

The initial empirical basis for this thesis was provided by Rook,[2] who found chloro- and bromo-THM compounds after treating peat extract and lake water from a peaty region with chlorine in the presence of bromide ion. To demonstrate that the humic acid building blocks could form THM, he reacted chlorine with resorcinol, dimedone, 1,3-cyclohexanedione and 1,3-indandione at pH 7.5 and 10°C and got 50 to 75 percent yields of chloroform. Furthermore, at pH 11, yields of 71 to 100 percent were obtained. Such enhancement in yield would be expected since the initial, slow step in the haloform reaction (Fig. 1) is an enolization or removal of an α proton, which occurs more rapidly at pH 11 than at pH 7.5. Chlorination of catechol, hydroquinone, pyrogallol, phloroglucinol (Fig. 2) and acetone produced traces of chloroform at pH 7.5 and yields of only 1 to 26 percent at pH 11. Apparently, the presence of meta hydroxy or keto groups provides sites for the haloform reaction.

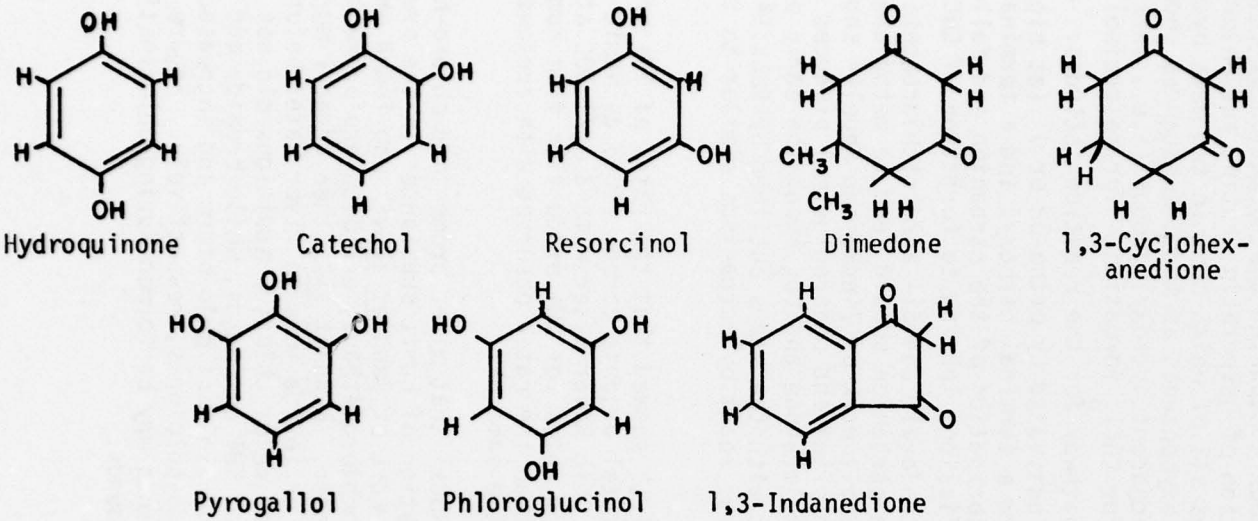


Figure 2. Structures of Some of the Compounds Which have been Shown to Produce Haloforms in References 3 and 10.

At high pH this reaction is catalyzed by base and the polyhydric phenols are converted into phenoxide anions, which are known to be very reactive toward electrophilic attack by chlorine in water.[11]

In a more recent paper, Rook[12] reported the formation of chloroform in high yields from chlorination of hesperetin, rutin, and phlorizin, three small natural glycosides all of which contain two meta hydroxyl groups. Chlorination of hydroxybenzenes as model substances showed that the carbon atom between two adjacent hydroxyl groups (i.e., meta-dihydroxy) is probably the active site for $CHCl_3$ formation. For resorcinol and fulvic acids the probable reaction pathway for the reaction includes: a) fast chlorination of carbon atoms activated by ortho-OH or O^- (at high pH), b) opening of the ring to form a terminal carboxyl and a terminal chlorocarbanion and, c) further chlorination of the carbanion end followed by oxidative and/or hydrolytic fission, leading to formation of $CHCl_3$, highly chlorinated acetones, chloral, and di- and trichloroacetic acids (Fig. 3). Protonation of the carbanion should lead to methylene chloride instead of chloroform. The early work of Zincke and Kegel[13] showed that the reaction of bromine or chlorine and phloroglucinol produced an octabromo- or octachloro-acetylacetone and CO_2 among the early products of the reaction, in agreement with the steps outlined by Rook.[12] Hence, bromine in aqueous solution may react by mechanisms similar to those shown for chlorine.

The work of Stevens et al.,[4] showed that the rates of THM production from chlorination of 5 mg/l total organic carbon (TOC) as humic acid at pH 7 and chlorination of raw Ohio River water with 3 mg/l TOC at pH 6.6 - 6.9 are similar. The observed rates for THM production from humic acid and river water were higher than the rates observed with acetone, acetaldehyde, and acetophenone at the same pH.

Initial observations by Rook[2] that mixed bromo- and chloro-haloforms were produced during chlorination of humic substances in the presence of bromide was supported by the work of Bunn et al.,[14] who found chloroform, bromodichloromethane, dibromochloromethane, and dichloroiodomethane in chlorinated Missouri River water. Bunn et al., then added 1 mg/l of fluoride, bromide, chloride, or iodide ions to river water before chlorination. They found that fluoride or chloride additions did not affect the relative concentrations of THM compounds, while bromide and iodide additions reduced the relative yield of chloroform and increased the proportions of bromo- and iodo-haloforms, respectively. Figure 1 (b) shows how other halogen oxidants may be formed during chlorination as precursors of mixed THM compounds.

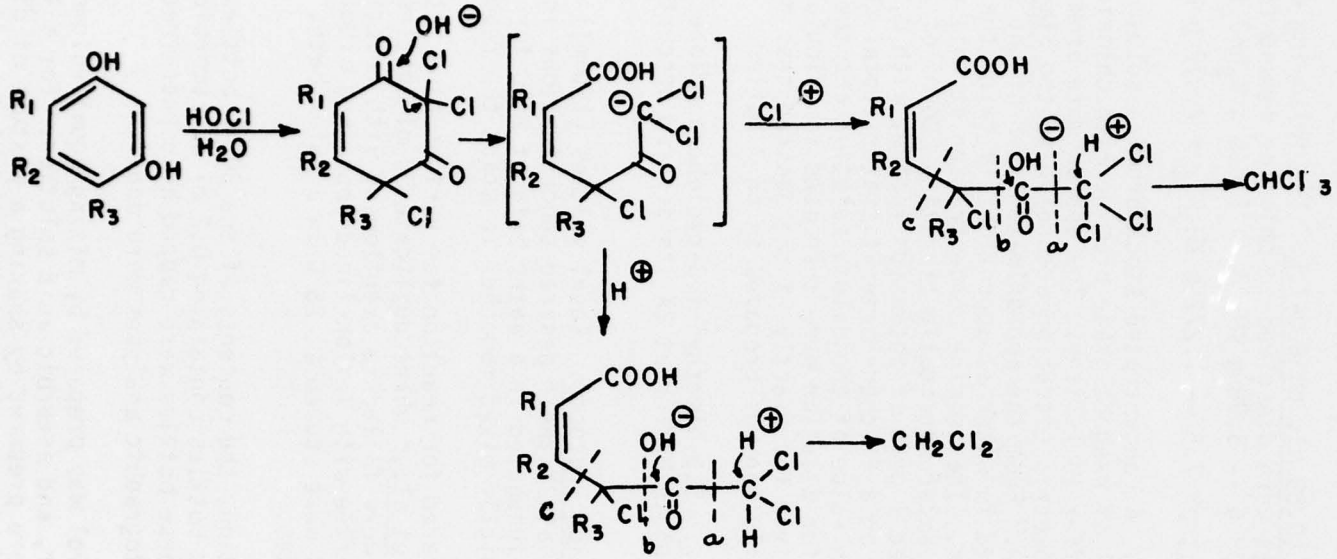


Figure 3. Proposed Degradation of Fulvic Acids and Resorcinol, According to Rook.[12] R_1, R_2, R_3 = fulvic acid matrix molecule or H, OH, OCH_3, or COOH.

MATERIALS AND METHODS

Phosphate Buffers (0.05 M), pH 6.0-7.5. The following quantities of ACS grade reagent salts were dissolved in chlorine demand-free water and diluted to 1 liter: pH 6 -- 5.98 g KH_2PO_4 + 1.045 g K_2HPO_4; pH 7 -- 2.86 g KH_2PO_4 + 5.05 g K_2HPO_4; pH 7.5 -- 1.272 g KH_2PO_4 + 7.072 g K_2HPO_4.

Bromine Solutions. A concentrated stock bromine solution was prepared by diluting 1 ml of reagent grade bromine with chlorine demand-free water or with pH 7 buffer to 1 liter. The approximate bromine concentration was found by iodometric titration according to the Standard Methods[15] procedure for chlorine. From the approximate titer of the stock solution, a dilution was prepared in water at approximately twice the desired test reaction concentration. The bromine concentration at this dilution was determined at pH 4 by amperometrically titrating 200 ml of the solution to which had been added 1 gram of potassium iodide, with 0.00564N phenylarsine oxide solution on a Fischer-Porter titrator (total chlorine mode). The true concentration value of the dilute solution and the volume of stock solution taken for dilution were then used to calculate the dilution of stock bromine required for exactly 2X the desired test reaction concentration. The exact dilution was prepared in pH 7 buffer.

Dimedone Solutions. 5,5-Dimethyl-1,3-cyclohexanedione (Eastman 1259) was dissolved in phosphate buffer at 2X its desired concentration for reaction.

Bromination Reaction Protocol. Equal volumes (150 ml) of dimedone and bromine solutions at 2X their desired concentrations in pH 7 buffer in the reaction were incubated in a water bath at 25°C for 30 minutes. The solutions were quickly mixed together to start the reaction.

Samples were prepared for reaction for various time intervals, by the procedure of Stevens et al.,[4] where duplicate 30 ml bottles for each reaction time period were filled to overflowing with reaction mixture and capped headspace-free with Teflon-lined septa and aluminum crimped sealers. The bottles were stored at 25°C in a water bath, generally for 30, 60, and 120 minutes.

To stop the reaction, the contents of the 30 ml bottles were transferred to 10 ml serum bottles containing 0.2 ml of ascorbic acid solution (8 g/100 ml H_2O). These bottles were capped headspace-free and stored at 4°C until gas chromatographic analyses were done.

A zero-time control was prepared by mixing equal volumes of dimedone solution, pH 7 buffer, and ascorbic acid solution. For a 1 minute reaction time, samples were prepared by shaking a mixture of dimedone and bromine solution for 1 minute, then pouring the mixture directly into 10 ml serum bottles containing ascorbic acid solution.

Stripping Apparatus. The apparatus described by Bellar and Lichtenberg[1] for stripping volatile compounds from 5 ml of water was used in these studies. As shown in Figure 4, a water sample could be introduced with the 5 ml syringe and later withdrawn completely by means of the Teflon tube which extended down to the glass frit of the stripping apparatus. The "open-close" valve of the syringe prevented escape of stripping gas back through the syringe during sample purging. All gases were thus routed through the foam trap and into the Tenax GC porous polymer trap. The entire apparatus was maintained intact for several samples. Only the Tenax trap was connected and disconnected for purging and backflush, respectively, of each sample. The trap was sealed into the 1/4-in. to 1/8-in. Swagelok reducing union on the foam trap by means of a 1/8-in. Swagelok nut, reversed 1/8-in. front ferrule and 1/8-in. ID O-ring.

Figure 5 shows the construction of the Tenax trap used to collect the volatile organics and to pass most of the water vapor stripped from the sample. The Speedaire Quick Connect (QC) stem was modified by boring out the pipe thread-Swagelok union to allow the trap tube to pass through the union.

The backflushing of trapped organic materials from the Tenax GC polymer trap onto the analytical column of the gas chromatograph (Hewlett-Packard 5750B) was accomplished with a small 1/4-in. diameter tube oven connected to the inlet port of the gas chromatograph (Fig. 4). A 1/8-in. port connector seated in a Swagelok 1/8-in. nut (soldered to the septum retainer nut, leak-tight) passed the gas stream from the backflushing oven through a hole in the rubber septum. A Nupro valve was used to open the gas chromatograph column inlet to the backflushing gases and to seal off the inlet after the backflushing step, during the GC analysis.

A leak-tight seal was formed by locking the Tenax trap QC stem into the QC body assembly attached to the backflushing oven. To allow passage of the trap through the QC body, the check valve and spring normally in the QC body were removed. The backflushing oven was heated with heating tape, which was wrapped around the tube oven. A thermister probe was inserted under the tape to provide temperature control signals to a Cole-Parmer Model 2157 temperature controller, which supplied current to the heating tape.

Gas Chromatography. To analyze a sample, the 10 ml serum bottle was first warmed to 25°C in a water bath. Part of the sample was used to rinse the 5 ml syringe, then the syringe plunger was removed and the barrel was filled to the top so the plunger could be replaced without trapping bubbles. Excess volume was displaced from the syringe until 5 ml remained. The syringe was then connected to its needle on the stripping apparatus, the helium purge gas was connected, and the Tenax trap was vented with a miniature QC stem inserted into the QC body at the top of the trap. The sample was injected into the stripping apparatus,

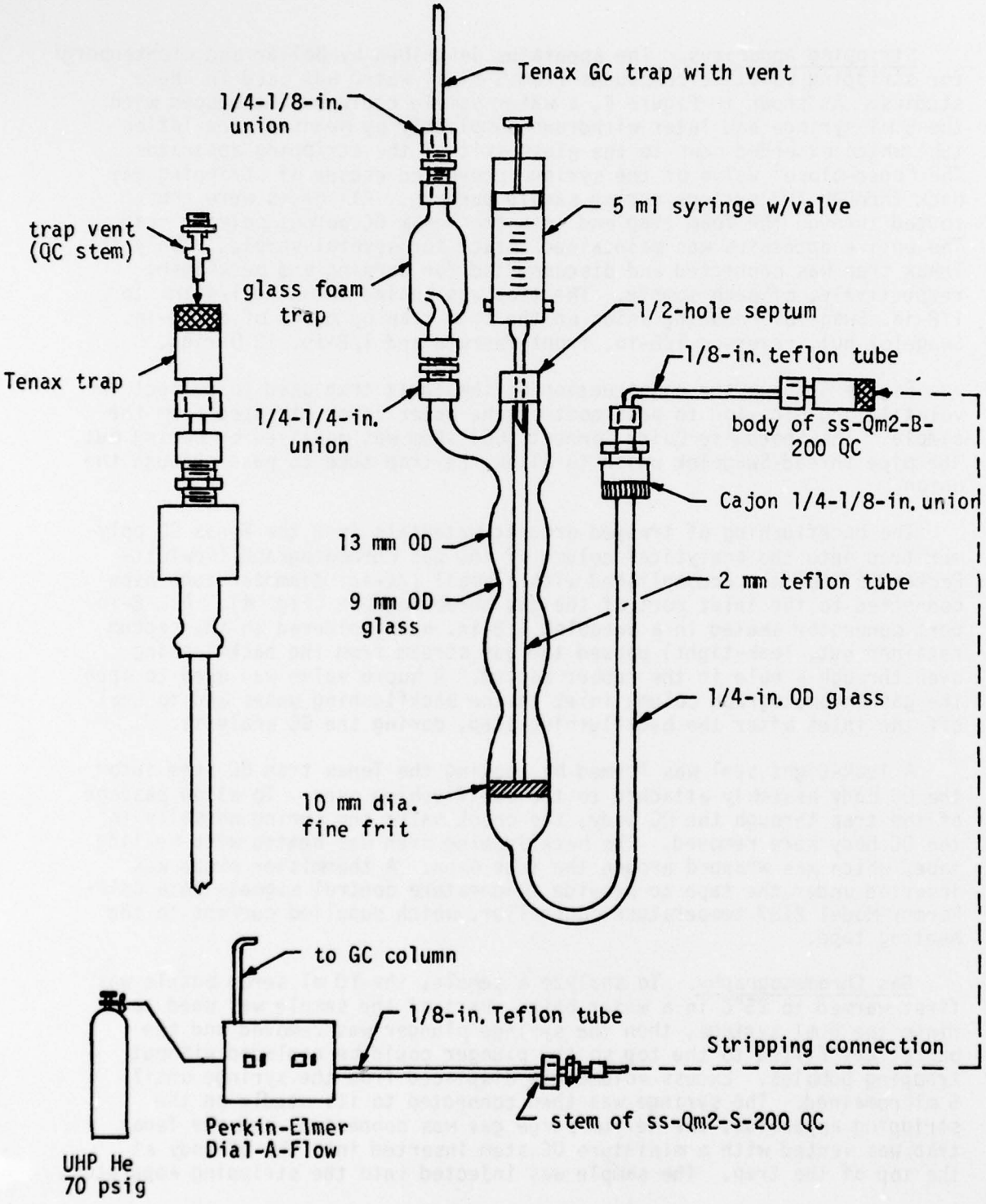
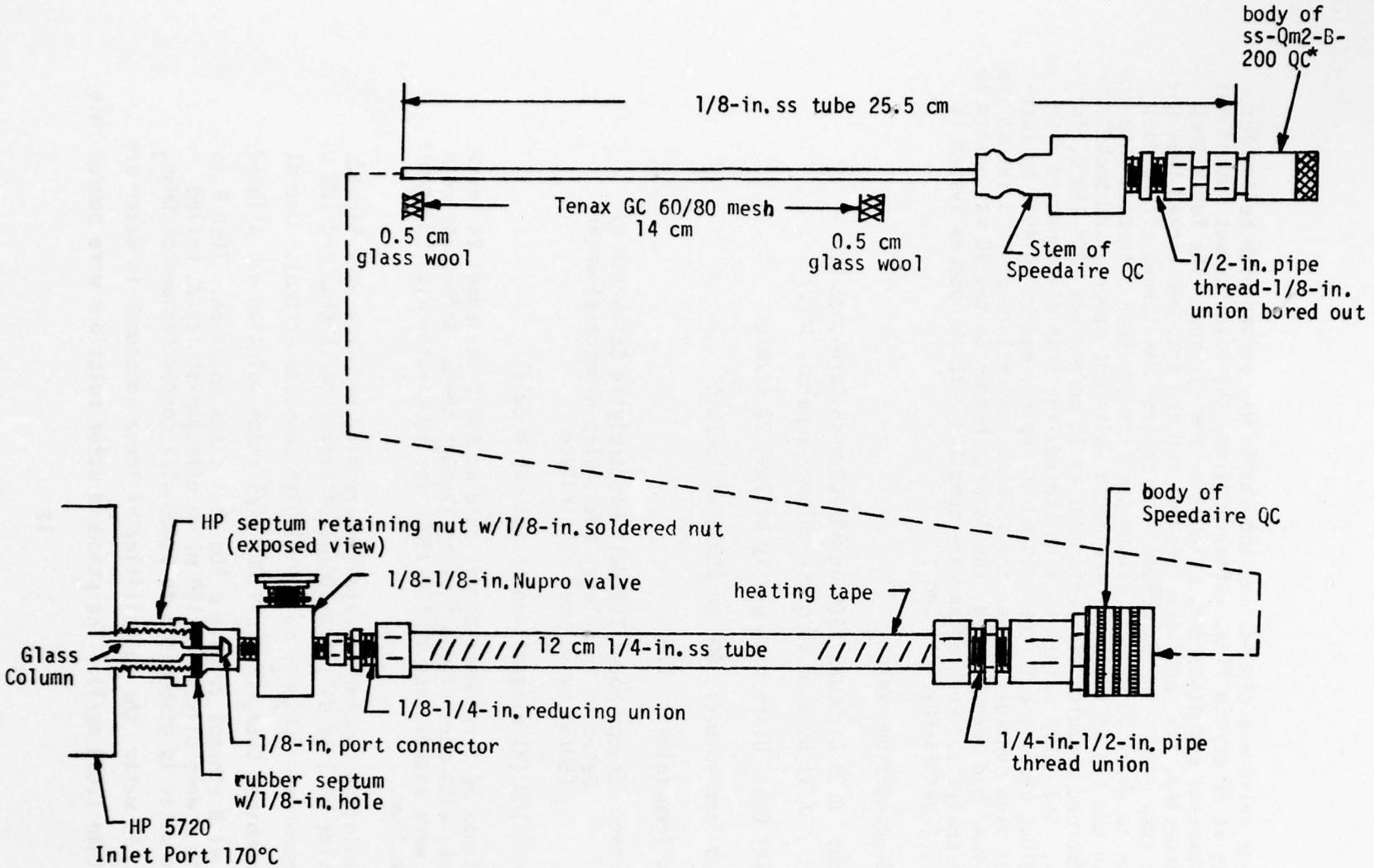


Figure 4. Details of Stripping Apparatus.



* Connected to a stem of a QC for venting gas during trapping mode; connected to stem of QC on He gas line for backflush. (QC = Quick Disconnect)

Figure 5. Details of Tenax Trap and Backflush Oven.

the syringe valve was closed, and the sample was purged with helium for 11 minutes at 20 cc/min flow. After purging, the solution was sucked out of the apparatus and discarded, using the same syringe. The Tenax trap was disconnected, its vent stem removed, and the trap was locked into the backflush tube oven. The GC column oven control was turned off to cool the column to about 30°C. The helium gas line was then connected into the QC body on the top of the trap, the Nupro valve was opened, and backflushing of adsorbed organics was performed, at 20 cc/min and 130°-150°C, for 3 minutes. The Nupro valve was then closed, the trap disconnected from the backflush oven, and the GC column was rapidly heated to 40°C by turning on the oven control. After the initial temperature of 40°C set on the GC programmer had been reached, the "start" button on the GC was pushed to begin the analysis. Peak areas were compiled with an AutoLab System IV integrator (Spectra-Physics, Inc.).

The GC conditions were:

Column: 0.2% Carbowax 1500 on 80/100 mesh Carbopack C, 6 ft by 2 mm ID glass column (Supelco, Inc.)

Carrier Gas: Ultra high purity helium, 22 cc/min

Column Temperature: 40° to 200°C at 15°/min

Inlet Temperature: 170°C

Detector: Tracor Model 700 Hall Electrolytic Conductivity Detector in halogen mode, with n-propanol-water (50/50 by volume) electrolyte

Range: 100 (X1 attenuation on AutoLab module)

New Tenax GC traps were conditioned at 300°C for about 24 hours before use, with carrier gas flowing through them. Before use each day they were backflushed at 130-150°C for 10 minutes with 20 cc/min of helium flow.

Quantitative combined standards were prepared from pure liquids (Chemservice kit) by diluting 100 µl of bromoform ($CHBr_3$) and 100 µl of dibromomethane (CH_2Br_2) to 100 ml with absolute ethanol. One ml of this combined $CHBr_3$-CH_2Br_2 1,000 µl/l stock solution was diluted to 10 ml with ethanol to give a 100 µl/l stock solution. Then 5 to 400 µl stock were diluted to 100 ml in nitrogen-stripped, boiled distilled water to give 0.005 to 0.400 µl/l concentrations of $CHBr_3$ and $CHBr_2$ in water (the solubilities of these compounds in water are greater than 1,000 mg/l). The standard water solutions were poured into

10 ml serum bottles containing 0.2 ml of ascorbic acid solution (8 g/100 ml) and refrigerated pending analysis.

Synthesis of Monobromodimedone (2-Bromo-5,5-dimethyl-1,3-cyclohexanedione)

Method #1. Dimedone (5 g, 0.036 moles) and 1 ml of water were transferred to a mortar and triturated while 5.7 g (0.036 moles) of liquid bromine were added dropwise. The reaction was highly exothermic yielding a brownish red, tacky mixture. After about 5 minutes the mixture was washed copiously with water and partially dried to give about 9 g of crude material. The crude material was recrystallized from aqueous ethanol (1:1). After the first crystallization, the product melted at 168-170°C and after the second, it melted at 170-172°C. Yield 8.0 g (75% theory).

Method #2. Dimedone (5 g, 0.036 moles), 25 ml of absolute ethanol, 25 ml of water and 1.91 g (0.018 moles) of Na_2CO_3 were mixed in a 200 ml round-bottom flask and equilibrated in an ice bath. A bromine solution, made by mixing 5.7 g of bromine, 25 ml of water and enough ethanol to give a clear solution, was gradually added to the ice cold mixture. (Absorption of bromine was very rapid -- the reaction occurred like a titration using a sharp indicator). After removal of water and ethanol by using a flash evaporator at about 15 mm of Hg, the residue was taken up in chloroform, washed with water and filtered. The chloroform was removed by evaporation, and the residue was treated with acetic acid, washed with water and recrystallized from absolute ethanol. After a second recrystallization, the product was collected and dried; m.p. 172-173°C, yield 8.9 g (84% theory).

Synthesis of Dibromodimedone (2,2-Dibromo-5,5-dimethyl-1,3-cyclohexanedione)

This compound was prepared by Method #2 above, except 11.4 g (0.074 moles) of bromine and 3.92 g (0.036 moles) of Na_2CO_3 were used per 5 g of dimedone. At the end of the addition of bromine, the reaction mixture had a pale amber color. Evolution of gas was vigorous. Crystals separated immediately. These were recrystallized from aqueous ethanol (1:2) yielding 12 g (74% theory), m.p. 143.5-144°C. This is a new synthesis. Literature values for melting points of monobromodimedone and dibromodimedone are 175°C and 144°C, respectively (Gupta and Thorpe).[16] The structures of the synthesized compounds were verified by mass spectrometry.

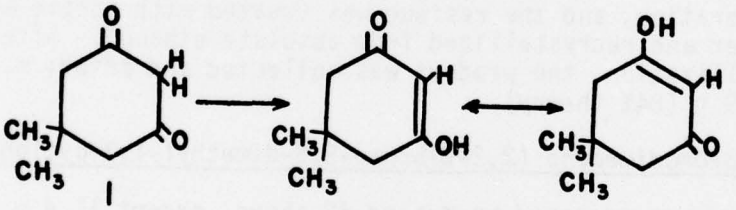
Reaction of Dibromodimedone with Water

Phosphate buffers (0.05 M) of pH 6, 7.0, and 7.5 (300 ml) were incubated at 25°C for at least 1/2 hour, and then spiked with 0.3 ml of a solution of 2,980 mg/l (1×10^{-2} M) dibromodimedone in acetonitrile to give a final concentration of 1×10^{-5} M. After 1 minute of mixing, samples were taken for quenching the reaction with ascorbic acid or for further reaction at 25°C in a water bath, by the same procedures described

above for dimedone bromination reactions. GC analyses were performed for CH_2Br_2 and $CHBr_3$. Parallel runs were made in which the solutions were poured into a 1 cm thermostated cuvette (25°C) in a Beckman Acta V recording spectrophotometer. UV scans from 260 to 300 nm were taken to follow the production of monobromodimedone at 292 nm with time. Solutions of monobromodimedone in water were used to calculate the molar absorptivity at each pH, for use in calculating monobromodimedone concentrations, assuming Beer's Law.

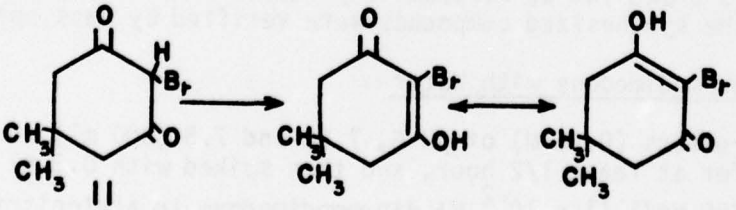
RESULTS AND DISCUSSION

Dimedone at pH 7 showed an absorbance maximum at 280 nm (Fig. 6). When equal volumes of 1.25×10^{-4} M bromine and 1×10^{-4} M dimedone were mixed, the absorbance maximum immediately shifted to 292 nm, and showed no further change between 2 minutes and 1.4 hours of reaction at 25°C. Attempts to follow the decrease in absorbance at 280 nm with time showed that the reaction was so rapid that the absorbance dropped to a constant level in less than 3 seconds after mixing the two reagents. The UV absorbance of dimedone (I) is due to two equivalent enolization structures (Equation 1).



(1)

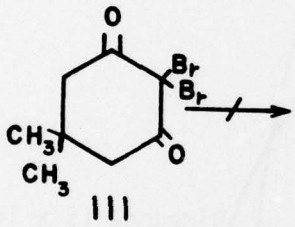
Replacement of a single hydrogen by a bromine to give monobromodimedone (II), would still allow two enolization structures to be drawn (Equation 2). Consequently, some UV



(2)

absorbance, although at a different wavelength, would still exist for monobromodimedone. Pure monobromodimedone did in fact show an absorbance peak at 292 nm, in agreement with the absorbance of the bromination reaction product shown in Figure 6.

When excess bromine was added by placing two drops of 2,800 mg/l bromine solution into the cuvette, the absorbance at 292 nm was reduced markedly (Fig. 7). There was no absorbance maximum between 220 and 340 nm, as is true for the absorbance spectrum of pure dibromodimedone, indicating that the monobromodimedone had been converted into the dibromodimedone, or that the reaction had opened the dimedone ring. The lack of a strong UV maximum in dibromodimedone (III) could be explained by the inability of this product to form a conjugated enone because both enol-forming hydrogens were replaced by bromine atoms (Equation 3):



no enolization (3)

III

GC analyses of bromine-dimedone reaction mixtures by the stripping-trapping procedure rather than by direct injection onto the GC column provided quantitation of actual trihalomethane concentrations in solution at 25°C, without interference from possible secondary production of THM compounds in the hot injection port of a GC during direct injection. Such positive interferences have been noted by other workers at USAMBRDL, who found that trichloroacetic acid produced chloroform upon direct injection.[17] Figure 8 shows typical standard curves for bromoform and dibromomethane by the stripping-trapping method. The curves were fitted using a second order polynomial $y = b_0 + b_1 x + b_2 x^2$ program on a desk calculator.

Figure 9 shows the rate of production of volatile compounds at pH 7, 25°C, and 1:1 ratio of bromine to dimedone (10^{-3} M). The concentration of bromoform was essentially unchanged after 30 minutes, at about 0.05 µl/l. Assuming a bromoform liquid density of 2.89 mg/µl, this is a concentration of only 0.144 mg/l or 5.7×10^{-7}M (mw = 253), giving a production of bromoform of 0.057% of theory. It should be noted that 10^{-3} M bromine is 160 mg/l, hence quite a high concentration compared to what might be

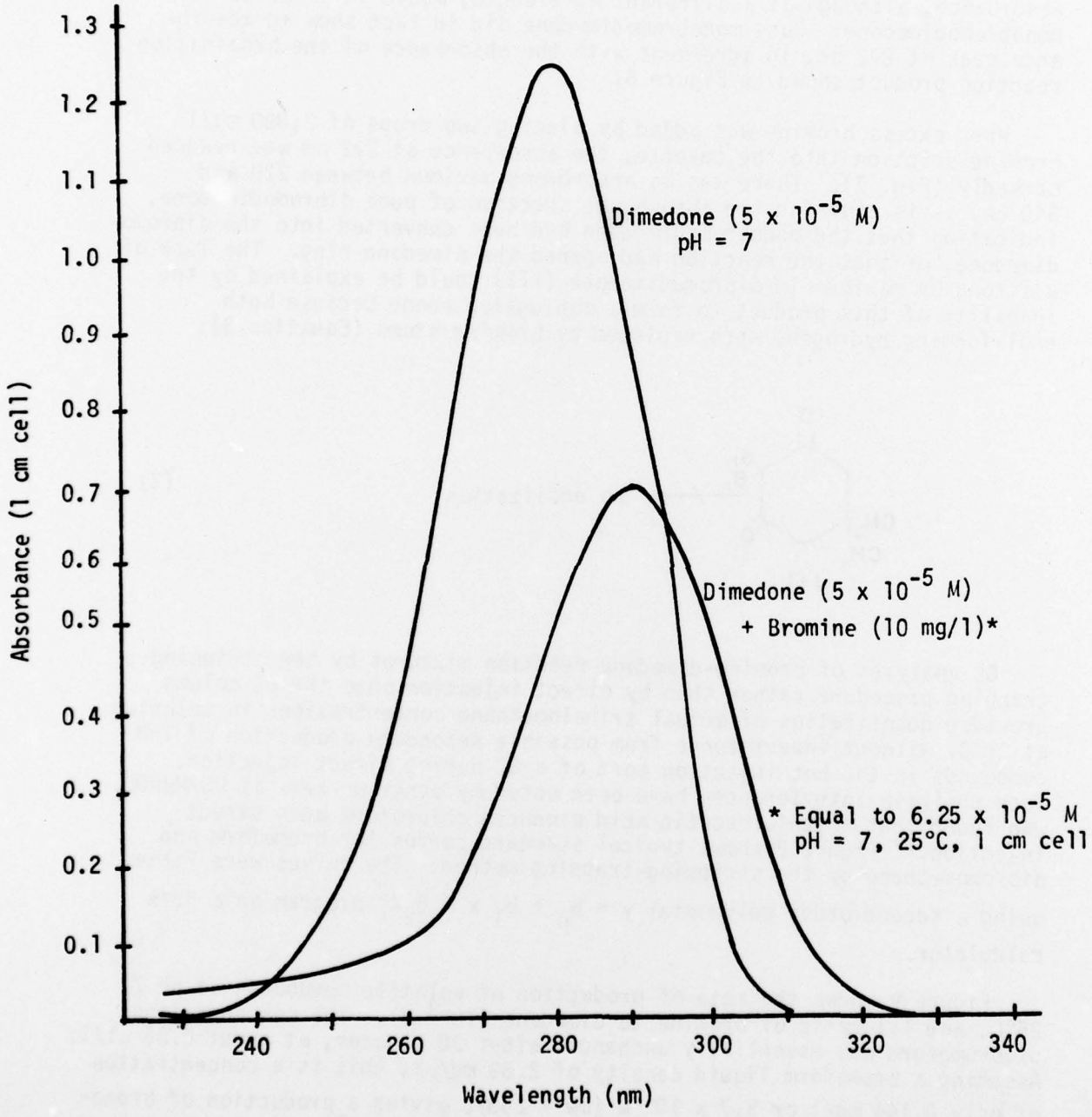


Figure 6. UV Spectrophotometric Scans of Dimedone and Brominated Dimedone

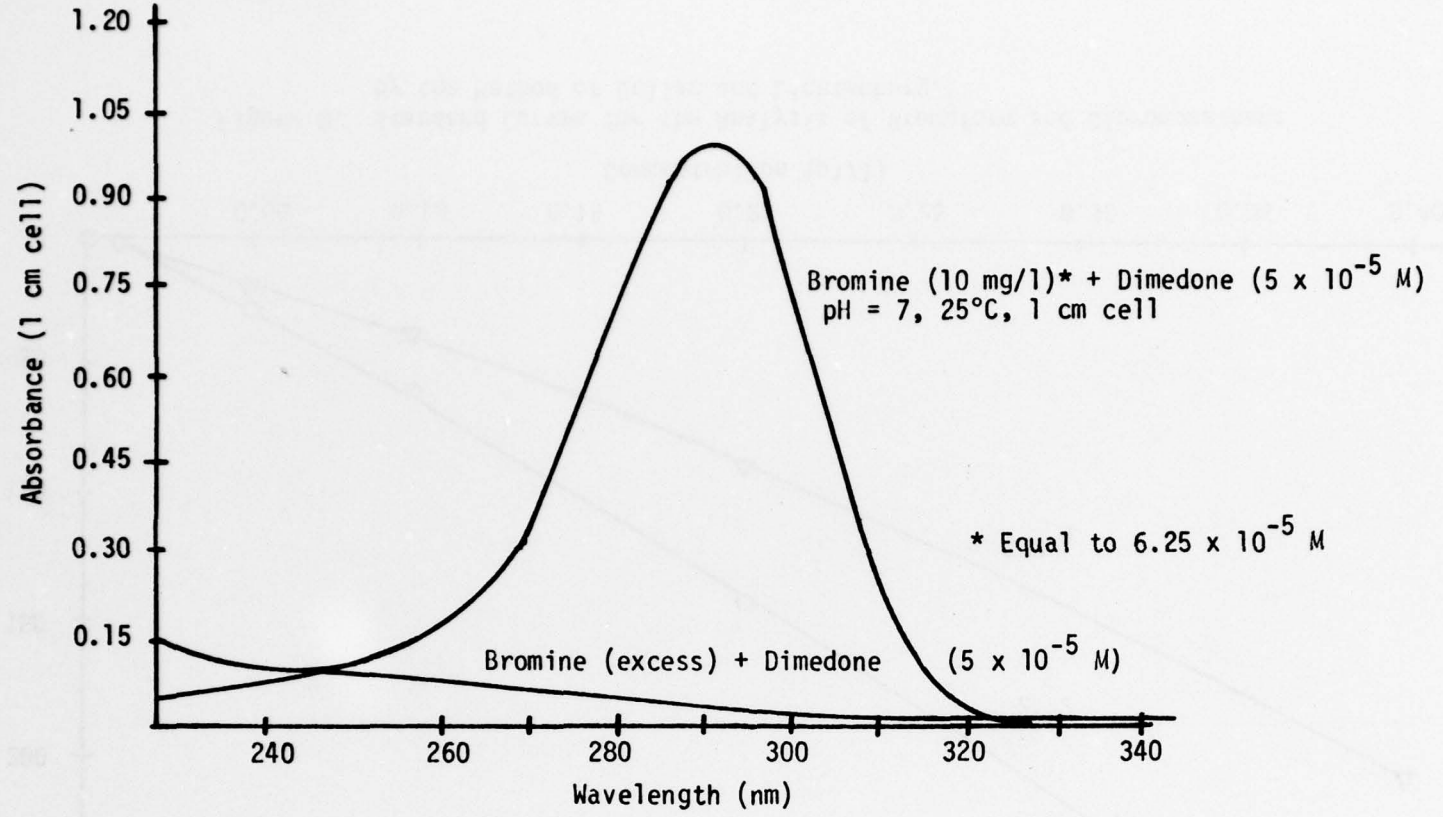


Figure 7. UV Spectrophotometric Scans of Dimedone Treated with Approximately Equivalent and Excess Amounts of Bromine.

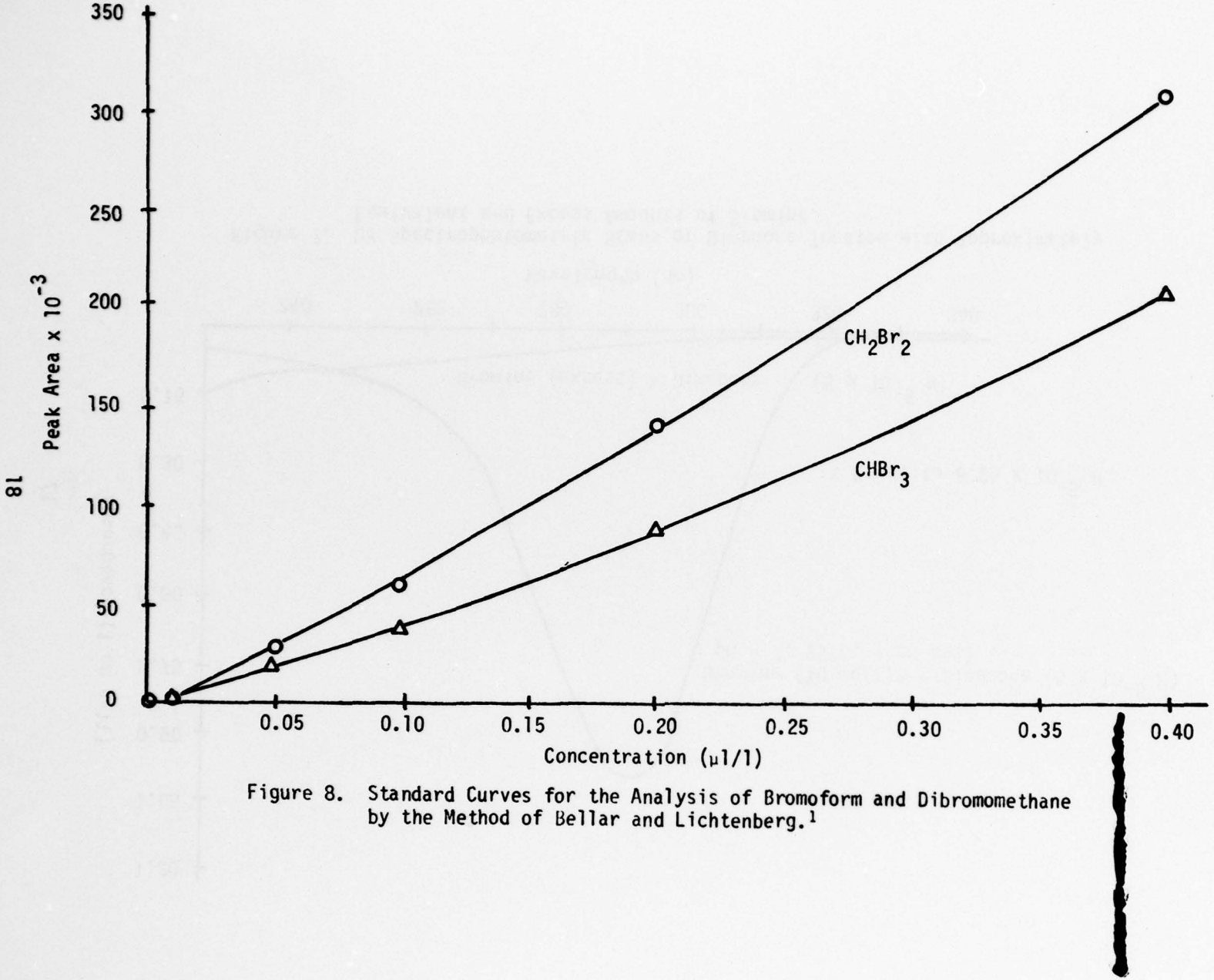


Figure 8. Standard Curves for the Analysis of Bromoform and Dibromomethane by the Method of Bellar and Lichtenberg.[1]

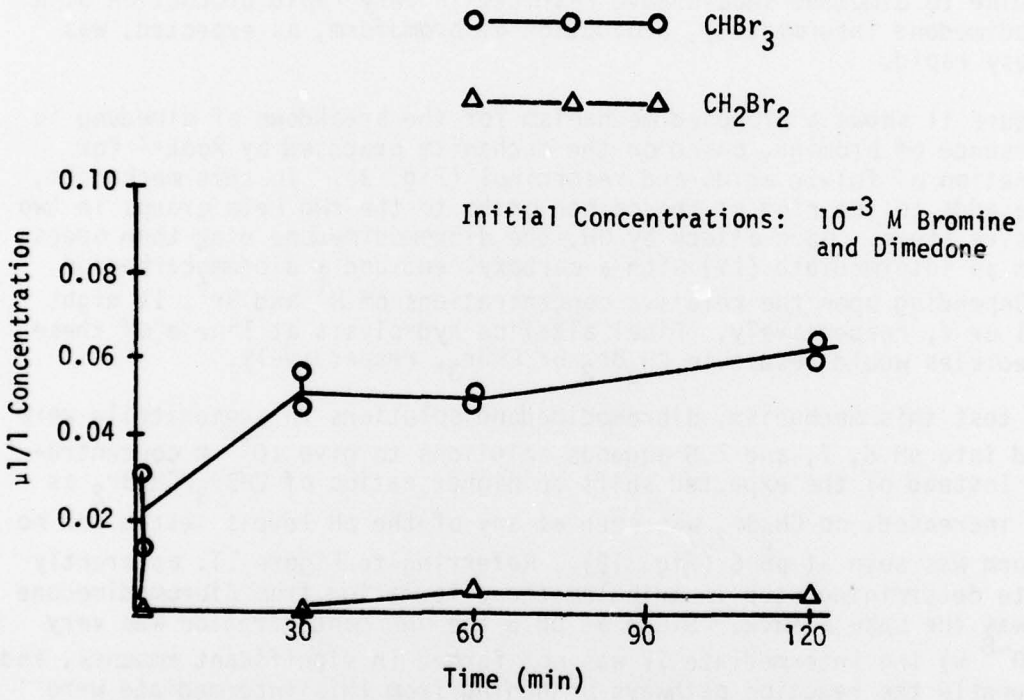


Figure 9. Trihalomethane Produced in the Reaction of Bromine and Dimedone at pH 7 and 25°C.

expected in wastewater disinfection (approximately 10 mg/l bromine). The low yield of bromoform and even lower yield of dibromomethane indicated that most of the reaction was probably the replacement of an enolic hydrogen by bromine to form monobromodimedone as demonstrated by UV data (Fig. 5). When the ratio of bromine to dimedone was increased to 2:1, the bromoform production increased by about 300-fold (Fig. 10). Assuming a final concentration of 14 µl/l or 40.5 mg/l, the yield was 1.6×10^{-4} M or 16 percent (assuming 1 mole of bromoform produced per mole of dimedone). When reaction samples required for the analysis of bromoform were diluted, the concentrations of dibromomethane were reduced to undetectable levels in the analysis and could not be plotted in Figure 9. Since the 2:1 ratio of bromine to dimedone should have resulted in very rapid production of a dibromodimedone intermediate, production of bromoform, as expected, was also very rapid.

Figure 11 shows a proposed mechanism for the breakdown of dimedone in the presence of bromine, based on the mechanism proposed by Rook[12] for chlorination of fulvic acids and resorcinol (Fig. 3). In this mechanism, bromine adds to the ring at the carbon ortho to the two keto groups in two successive steps. Upon attack by OH^-, the dibromodimedone ring then opens to form an intermediate (IV) with a carboxyl end and a dibromocarbanion end. Depending upon the relative concentrations of H^+ and Br^+, IV might form VI or V, respectively. Final alkaline hydrolysis at line a of these intermediates would result in CH_2Br_2 or $CHBr_3$, respectively.

To test this mechanism, dibromodimedone solutions in acetonitrile were diluted into pH 6, 7, and 7.5 aqueous solutions to give 10^{-5} M concentration. Instead of the expected shift to higher ratios of $CHBr_3/CH_2Br_2$ as the pH increased, no CH_2Br_2 was seen at any of the pH levels tested and no bromoform was seen at pH 6 (Fig. 12). Referring to Figure 11, apparently the rate determining step in trihalomethane formation from dibromodimedone (III) was the base attack. Since at pH 6 the OH^- concentration was very low (10^{-8} M) the intermediate IV was not formed in significant amounts, and consequently the reaction pathways branching from this intermediate were also slowed significantly. As the pH increased, the production of $CHBr_3$ (from reaction of IV with Br^+ produced by dibromodimedone itself) increased and the CH_2Br_2 remained undetectable, as expected from the low levels of H^+ available for reaction to form VI. At higher pH, VI would of course be subject to proton loss to form the anion, IV. Consequently the protonation pathway could not even be reached at low pH values, and at higher pH values it would not be important because of formation and removal of the anion IV to form $CHBr_3$ by bromination. The very low levels of CH_2Br_2 found at pH 7, when dimedone was brominated at a 1:1 molar ratio of bromine:dimedone support this thesis (Fig. 9).

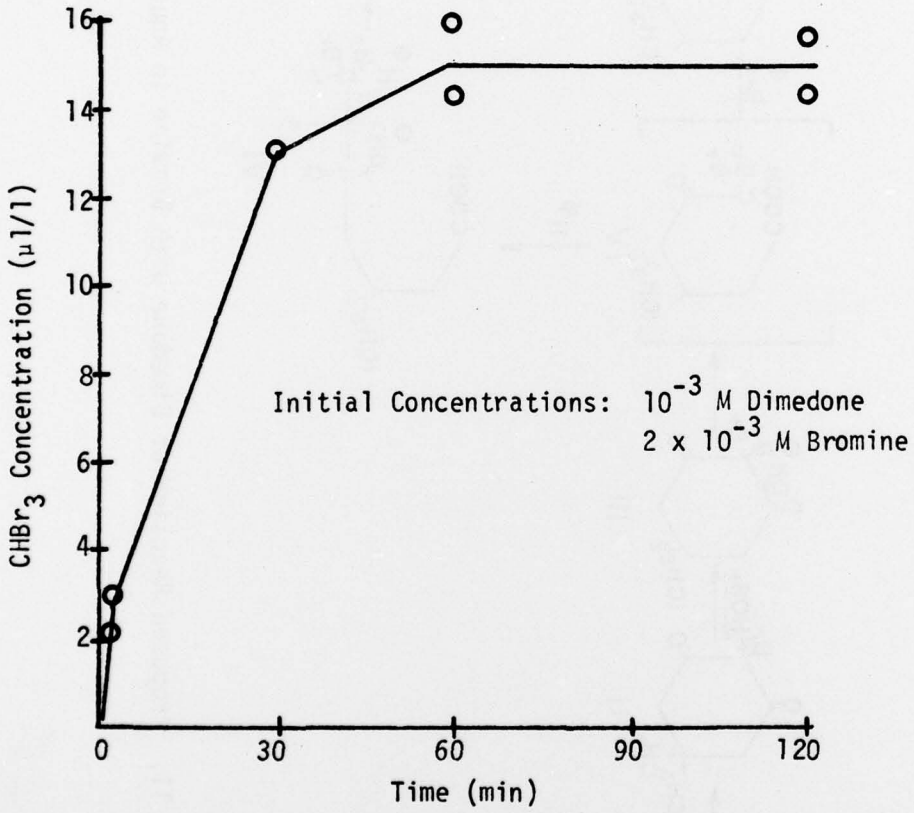


Figure 10. Bromoform Produced in the Reaction of Bromine and Dimedone at pH 7 and 25°C (2:1 ratio of Bromine to Dimedone).

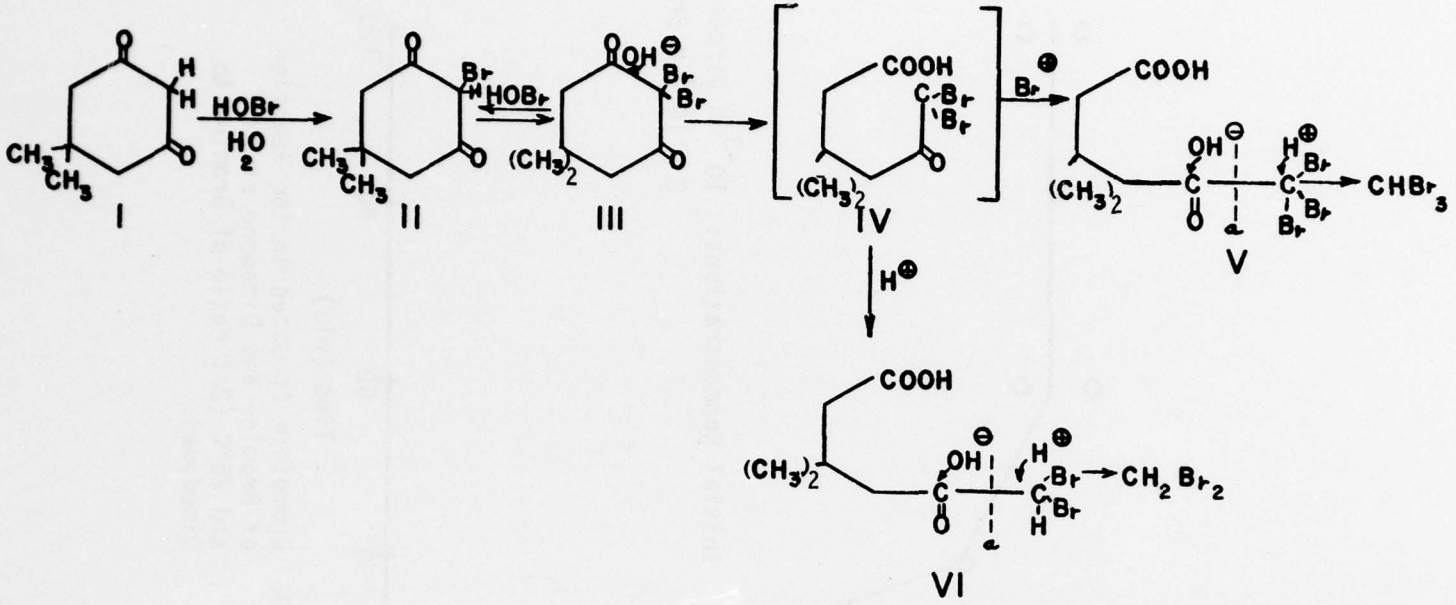


Figure 11. Proposed Reaction of Dimedone with Bromine in Aqueous Solution.

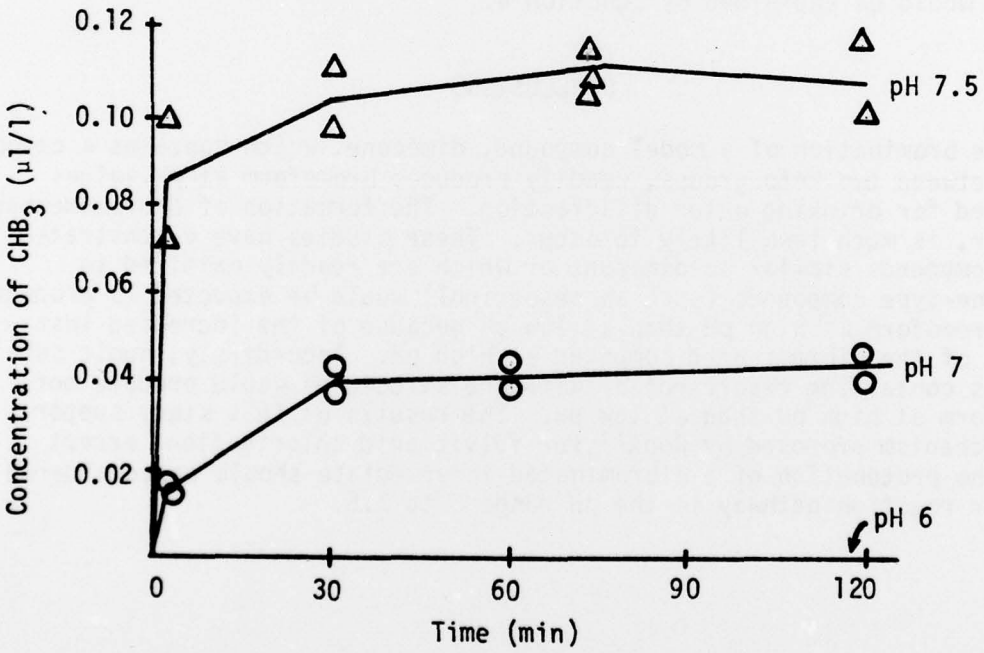
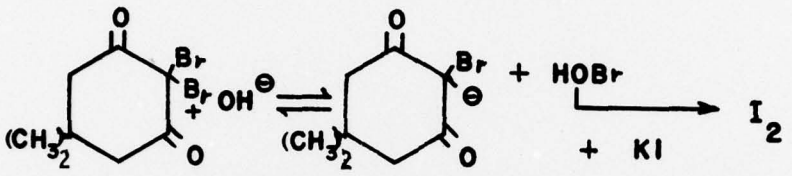


Figure 12. Bromoform Produced from 10^{-5} M Dibromodimedone at pH 6.0 to 7.5.

Calculations of monobromodimedone concentrations from UV absorbance data taken during dibromodimedone stability tests are presented in Figure 13. These data show that dibromodimedone is unstable in water and exists in equilibrium with monobromodimedone, as reported also by Norris and Thorpe,[18] and shown by positive reaction with potassium iodide:



(4)

The HOBr would be able to react with anion (IV) to produce $CHBr_3$. The higher concentration of monobromodimedone in equilibrium at higher pH values would be explained by Equation 4.

CONCLUSIONS

The bromination of a model compound, dimedone, which contains a carbon atom between two keto groups, readily produces bromoform at pH values expected for drinking water disinfection. The formation of dibromomethane, however, is much less likely to occur. These studies have demonstrated that compounds similar to dimedone or which are readily oxidized to dimedone-type compounds (such as resorcinol) would be expected to produce more bromoform at high pH than at low pH because of the increased instability of the dibrominated compound at high pH. Accordingly, humic substances containing resorcinol or dimedone structures would produce more bromoform at high pH than at low pH. The results of this study support the mechanism proposed by Rook[12] for fulvic acid chlorination, except that the protonation of a dibrominated intermediate should be considered a minor reaction pathway in the pH range 6 to 7.5.

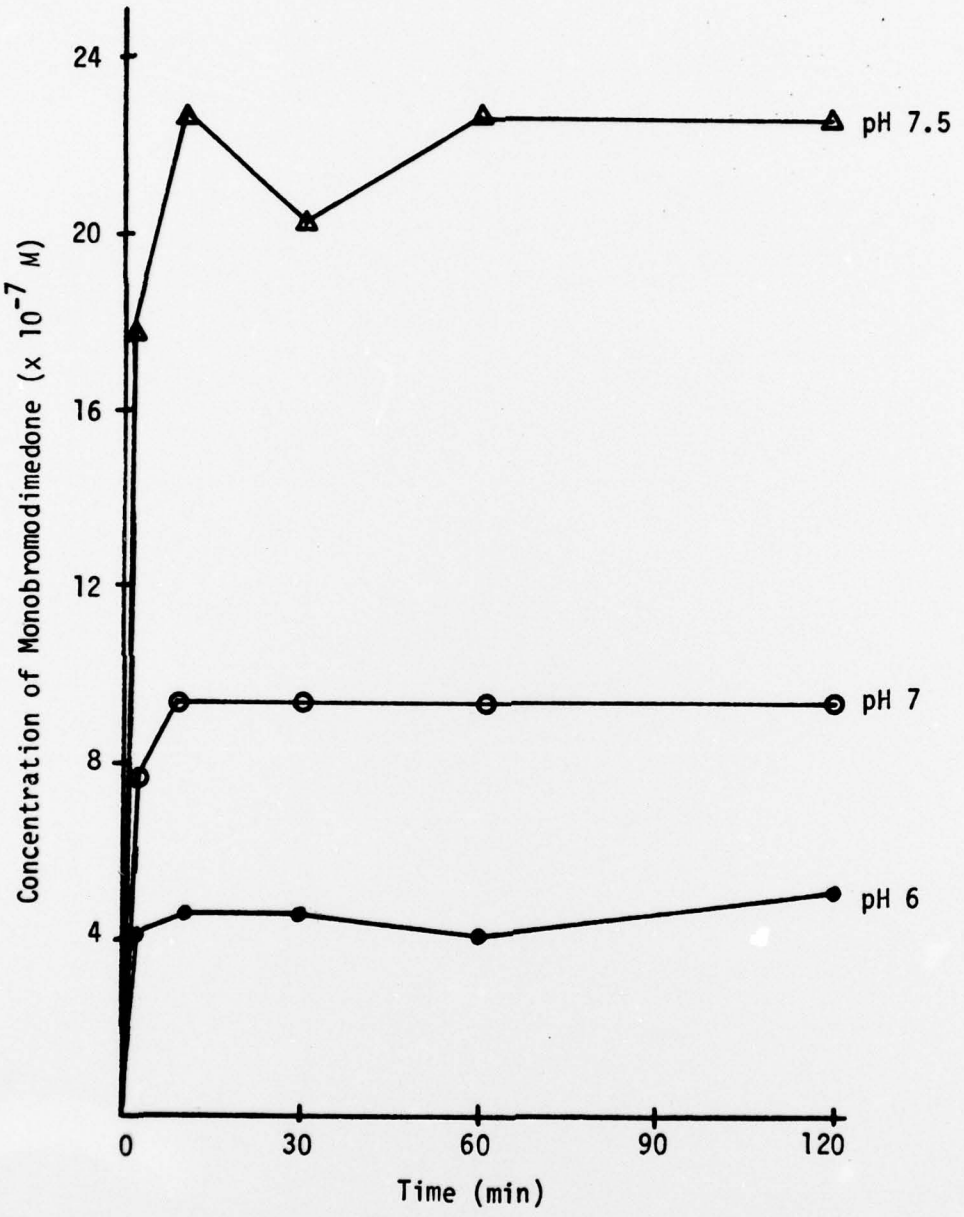


Figure 13. Monobromodimedone Produced from 10^{-5} M Dibromodimedone at pH 6.0 to 7.5.

LITERATURE CITED

1. Bellar, T. and J.J. Lichtenberg, "The Determination of Volatile Organic Compounds at the µg/l Level in Water by Gas Chromatography," U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, OH (EPA-670/4-74-009) (Nov 1974).

2. Rook, J.J., "Formation of Haloforms During Chlorination of Natural Waters," J. Water Treatment Exam., 23:234-243 (1974).

3. Rook, J.J., "Haloforms in Drinking Water," J. Am. Water Works Assoc., 68:168-172 (1976).

4. Stevens, A.A., C.J. Slocum, D.R. Seeger and G.G. Robeck, "Chlorination of Organics in Drinking Water," Presented at Conference on the Environmental Impact of Water Chlorination, Oak Ridge National Laboratory, Oak Ridge, TN (October 22-24, 1975).

5. Bellar, T.A., J.J. Lichtenberg and R.C. Kroner, "Organohalides in Chlorinated Drinking Waters," J. Am. Water Works Assoc., 66:703-706 (1974).

6. Dowty, B.J., R.R. Carlisle and J.L. Laseter, "New Orleans Drinking Water Sources Tested by Gas Chromatography-Mass Spectrometry," Environ. Sci. Technol., 9:762-765 (1975).

7. Symons, J.M., T.A. Bellar, J.R. Carswell, J. DeMarco, K.L. Kropp, G.G. Robeck, D.R. Seeger, C.J. Slocum, B.L. Smith and A.A. Stevens, "National Organics Reconnaisance Survey for Halogenated Organics," J. Am. Water Works Assoc., 67:634-647 (1975).

8. Dowty, B.J., D. Carlisle and J.L. Laseter, "Halogenated Hydrocarbons in New Orleans Drinking Water and Blood Plasma," Science, 187:75-77 (1975).

9. Kleopfer, R.D. and B.J. Fairless, "Characterization of Organic Components in a Municipal Water Supply," Environ. Sci. Technol., 6:1036-1037 (1972).

10. Booth, H. and B.C. Saunders, "The Iodoform Reaction," Chem. Ind., pp. 824-825 (23 December 1950).

11. Lee, G.F., "Kinetics of Reactions Between Chlorine and Phenolic Compounds," In: Principles and Applications of Water Chemistry, (Eds.) S.D. Faust and J.V. Hunter, John Wiley & Sons, New York, pp. 54-72 (1967).

12. Rook, J.J., "Chlorination Reactions of Fulvic Acids in Natural Waters," Environ. Sci. Technol., 11:478-482 (1977).

13. Zincke, Th. and O. Kegel, "Ueber Die Einwirkung von Brom and Phloroglucin," Chemische Berichte, 23:1706-1732 (1890).

14. Bunn, W.W., B.B. Haas, E.R. Deane and R.D. Kleopfer, "Formation of Trihalomethanes by Chlorination of Surface Water," Environ. Letters, 10:205-213 (1975).

15. Standard Methods for the Examination of Water and Wastewater, 14th Ed., American Public Health Association, Washington, DC (1976).

16. Gupta, B.M. and J.F. Thorpe, "The Formation of Bromine Derivatives of Carbon Compounds Without the Production of Hydrogen Bromide," J. Chem. Soc. (London), 121:1896-1904 (1922).

17. Meier, E.P., Personal Communication (1977).

18. Norris, W.S. and J.F. Thorpe, "The Formation and Stability of Spiro-Compounds. Part V. Derivatives of Cyclohexanespirocyclohexane and of Cyclopentanespirocyclohexane," J. Chem. Soc. (London), 119:1199-1210 (1921).

DISTRIBUTION LIST

Project No. 3A161101A91C/00/302

No. of Copies	
5	US Army Medical Research and Development Command ATTN: SGRD-AJ Fort Detrick, Frederick, MD 21701
12	Defense Documentation Center ATTN: DDC-PCA Alexandria, VA 22314
1	Academy of Health Sciences, US Army ATTN: AHS-COM Fort Sam Houston, TX 78234
2	USAMBRDL Technical Library
2	Chemical Systems Laboratory ARRADCOM Aberdeen Proving Ground, MD 21010